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Comparison Of Structural, Spectral And Thermal Properties Of Pure And L-Cystein Doped Bis Thiourea Cadmium Acetate (L-BTCA)

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abstract: *Nonlinear optical single crystals of pure and L-cystein doped bis thiourea cadmium acetate were grown by slow evaporation technique at room temperature with water as solvent. The crystalline nature was confirmed by powder X-ray diffraction analysis (XRD). The elemental composition was analysed by CHN study.The elemental confirmation of crystals was performed by using energy-dispersive X-ray analysis(EDAX). The structure and morphology of these crystals were studied by scanning electron microscopy (SEM) Fourier transform infrared (FTIR) studies confirm the various functional groups present in the crystals. The second harmonic generation efficiency was determined using Kurtz powder technique. The thermal behavior of the grown crystals has been investigated by DTA and TGA analysis.*
Keywords *- Crystal Growth, BTCA, L-BTCA*

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I. INTRODUCTION

The In recent years, organometalic non linear optical (NLO) materials have attained immense appeal from researchers due to a range of their technological applications in photonic field [1]. Bis thiourea cadmium acetate is one of the important organometalic non linear optical crystal because both organic and inorganic components in it contribute specifically to the process of Second Harmonic Generation [1-4]. A large family of thiourea metal complexes include zinc thiourea sulphate (ZTS), zinc thiourea chloride (ZTC), copper thiourea chloride (CTC), bis thiourea zinc acetate (BTZA), bis-thiourea cadmium acetate (BTCA), bis thiourea cadmium formate (BTCF), potassium thiourea chloride (PTC), potassium thiourea bromide (PTB) and potassium thiourea iodide (PTI) has been reported in literature [2-10]. L-Cystein the smallest naturally occurring aminoacid with a thiol group offers a high degree of chirality due to the presence of three different functional groups[11].It has Zwitter ionic state in aqueous solution as well as in solid state.[12]

This present work deals with growth of pure bis thiourea cadmium acetate and L-cystein doped bis thiourea cadmium acetate single crystals and their characterization by Powder XRD, CHN, EDAX, SEM,FTIR, thermal and NLO studies.

II. Experimental Details

BTCA salt was synthesized by dissolving cadmium acetate and thiourea in deionized water in the molar ratio 1:2 according to the reaction:

$2[CS(NH2)2] + Cd(C2H3O2)2 \rightarrow Cd[CS(NH2)2]2\ (C2H3O2)2$

The supersaturated solution of the synthesized salt was stirred well for 6 hours to yield a homogenious solution using magnetic stirrer. The solution was filtered using whatman filter paper and kept for evaporation at room temperature. The same procedure was applied to grow L-cystein doped crystals by adding 2 wt% concentration of L-cystein to the mother solution . Single crystals of pure and L-cystein doped BTCA were harvested in a period of 20-25 days. The purity of the synthesized salt was improved by successive recrystallisation process.

The grown crystals are shown in figure. 1

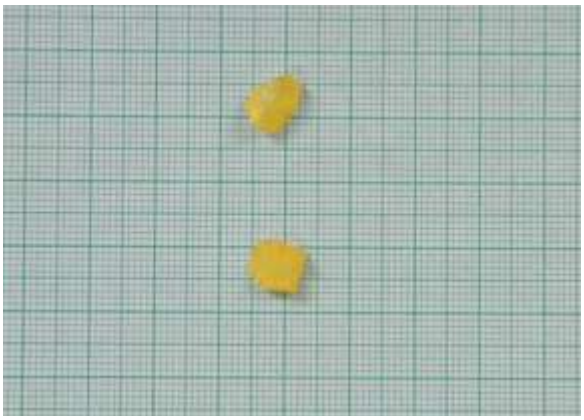


Fig 1: Photograph of Pure and L- BTCA single crystals

III. Results And Discussion

3.1 Powder XRD

XRD is the primary tool for determining the phase of a crystalline material. The structural characteristics were done by X-ray powder diffraction method, using Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λ=1.5406 Å, X-ray tube voltage = 40 kV and current = 35 mA). The scan was taken in the 2θ range from 0 - 80^0 at increments of 0.02° with a step time of 65.5 s. The powder diffraction patterns of pure and L-cystein doped BTCA are shown in figure 2. The sharp and well defined Bragg peak at specific 2θ value in the powder XRD pattern confirms their crystallinity.

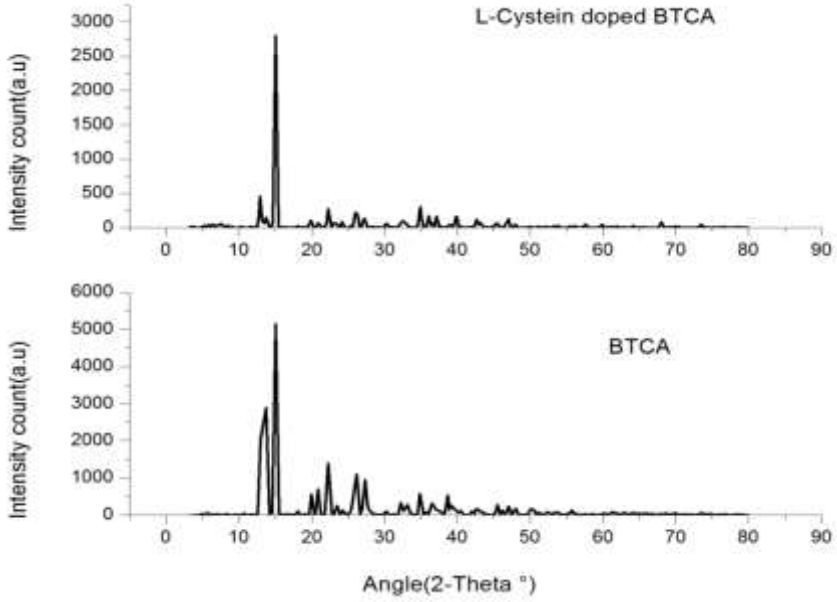


Fig 2: Powder XRD pattern of pure and doped BTCA

3.2 CHN Analysis

The elemental composition percentage of BTCA and L-cystein doped BTCA crystals were analyse using Elementar Vario EL III elemental analyser. The experimental C, H and N percentages were given in the Table 1.

Elements	Pure BTCA(%)	Doped BTCA (%)
Carbon	18.601938	17.935753
Hydrogen	3.624743	3.618581
Nitrogen	15.030819	15.490542
Sulphur	16.688019	18.419638

Table 1: CHN analysis of pure and doped BTCA

3.3 EDAX Analysis

It is a technique used for identifying the elemental composition of the specimen. The EDAX spectrum of both pure and L-cystein doped BTCA are shown in the Figure 3. All the prominent peaks corresponding to different elements in the sample were seen in the spectrum . The higher the peak in the spectrum, the more concentrated the element is in the specimen. The elevation in the peak of oxygen and sulphur elements show the incorporation of L-Cystein in the grown crystal.

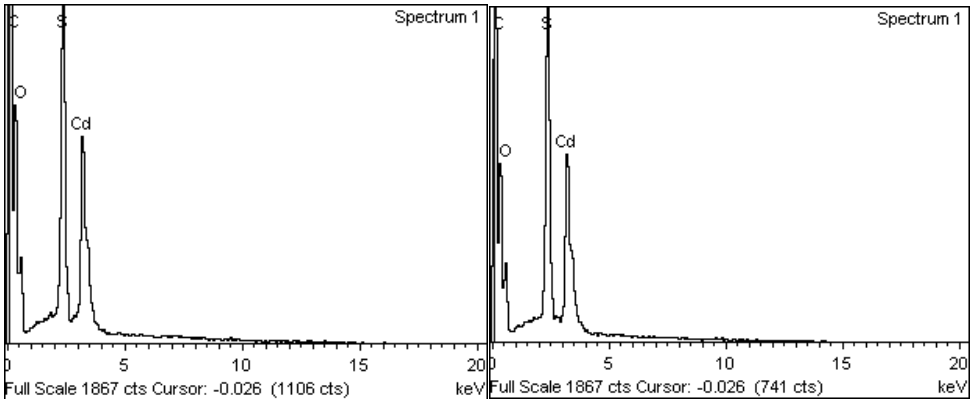


Fig 3. EDAX spectrum of pure and L-cystein doped BTCA

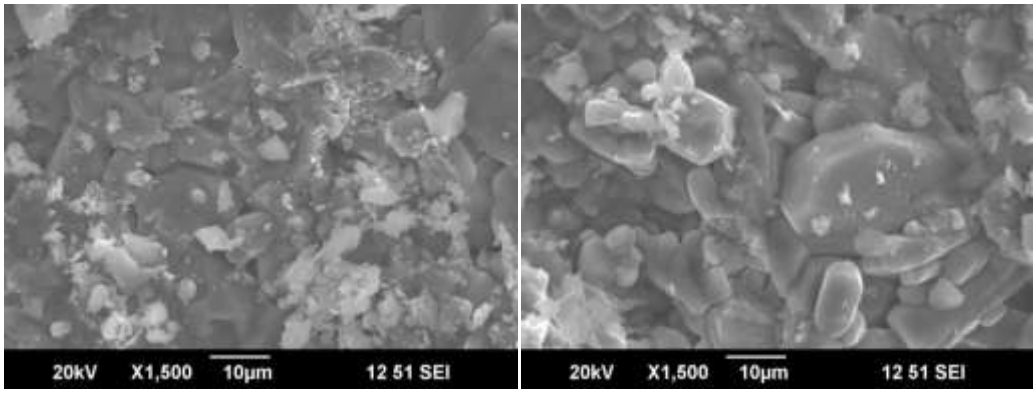
The Stchiomatric ratio of every element of pure and doped BTZA crystal are given in Table 2.

Crystal	Element	Weight %	Atomic %
BTCA	C	46.50	65.60
	O	24.47	25.92
	S	10.86	5.74
	Cd	18.16	2.74
L-cystein doped BTCA	C	42.94	62.74
	O	25.19	27.63
	S	11.89	6.51
	Cd	19.98	3.12

Table 2: stchiomatric ratio of element of pure and doped BTCA crystals

3.4 Scanning Electron Microscopy

The surface morphology of samples were analyzed with a scanning electron microscope JEOL MODEL JSM-6390LV, operating at 20 kV. The SEM photographs are shown in figure 4.



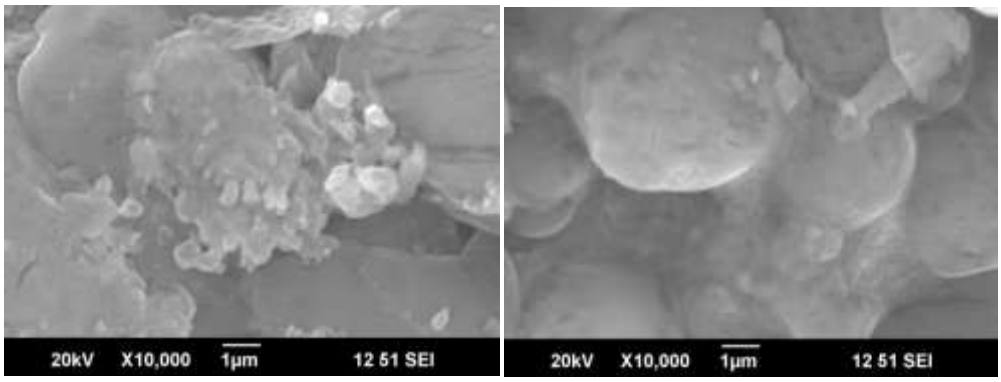


Fig 4: SEM image

s of Pure and doped BTCA crystal

From the photograph it can be concluded that the surface of the doped crystal is smooth compared to the pure sample which confirms that it can add more molecules to grow it to a large crystal.[13]

3.5 Thermal studies

Thermal analysis are used to find out the weight loss , melting and decomposition point of the grown crystals. Thermal behavior of the sample was analyzed by thermogravimetric analyzer (TGA) and differential thermal analyzer (DTA) using Perkin Elmer STA 6000, heating from ambient to 700 °C at a rate 10°C/min. The TGA/DTA curves of pure and doped BTCA are shown in figure 5.

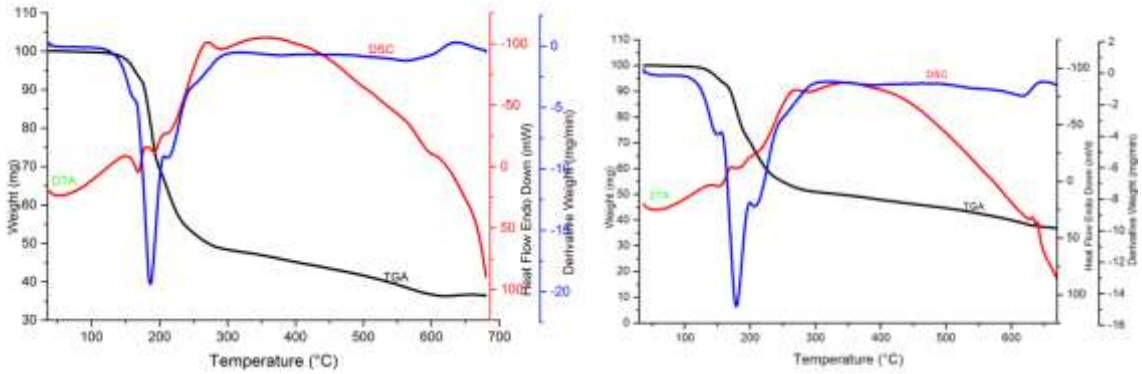


Fig 5: TG/DTA/DSC curves of pure and doped BTCA

The TGA curve of pure BTCA indicates that it is stable up to 140 ^{o}C which shows the crystal rejected solvent molecules during crystallization. The weight loss occurred in two steps .The major weight loss of 73 % take place between 150 ^{o}C to 280 ^{o}C due to the decomposition of the compounds and the second loss of 18% between 280 ^{o}C to 600 ^{o}C due to the organic solvent evaporation. Differential thermal analysis confirms through a sharp exothermic peak at 186.5 ^{o}C which corresponds to the melting point of the sample.The TGA curve of L-cystein doped BTCA is stable up to 130 ^{o}C . The major weight loss of 79 % take place between 100 ^{o}C to 300 ^{o}C and the second loss of 28% between 300 ^{o}C to 600 ^{o}C. The melting point is shifted to 189.30 ^{o}C when doped with 2 wt% of L-Cystein.

3.6 FTIR

Fourier transform infrared (FTIR) spectra of the pure and L- cystein doped BTCA were recorded by FTIR spectrophotometer (Thermo Nicolet, Avatar 370) in the range 4000 to 400cm^{-1} by KBr pellet technique and the spectras are shown in figure 6 and 7. The modes of vibrations of bis thiourea cadmium acetate are assigned and presented in the table 3.

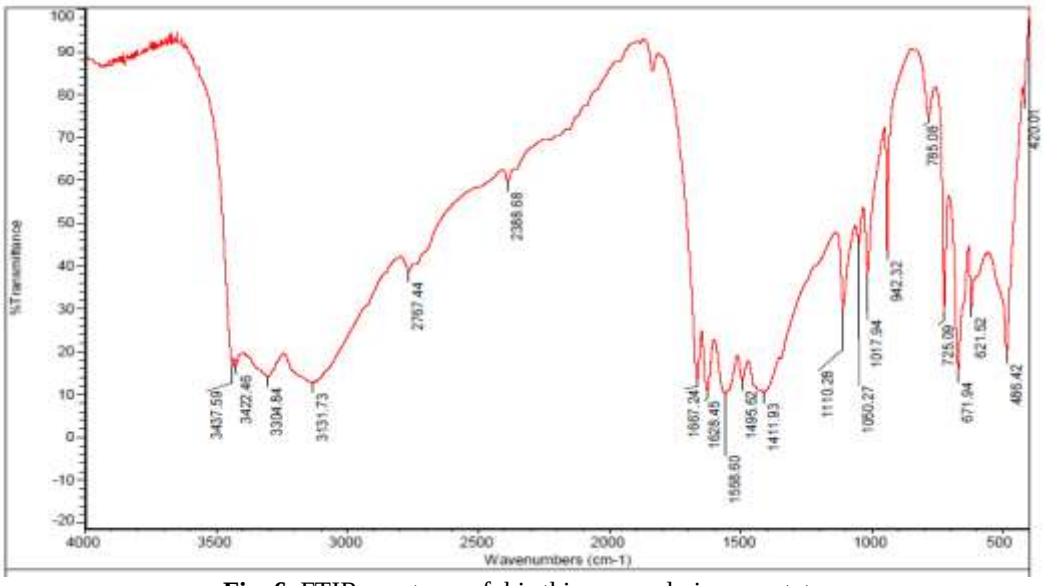


Fig. 6. FTIR spectrum of bis thiourea cadmium acetate

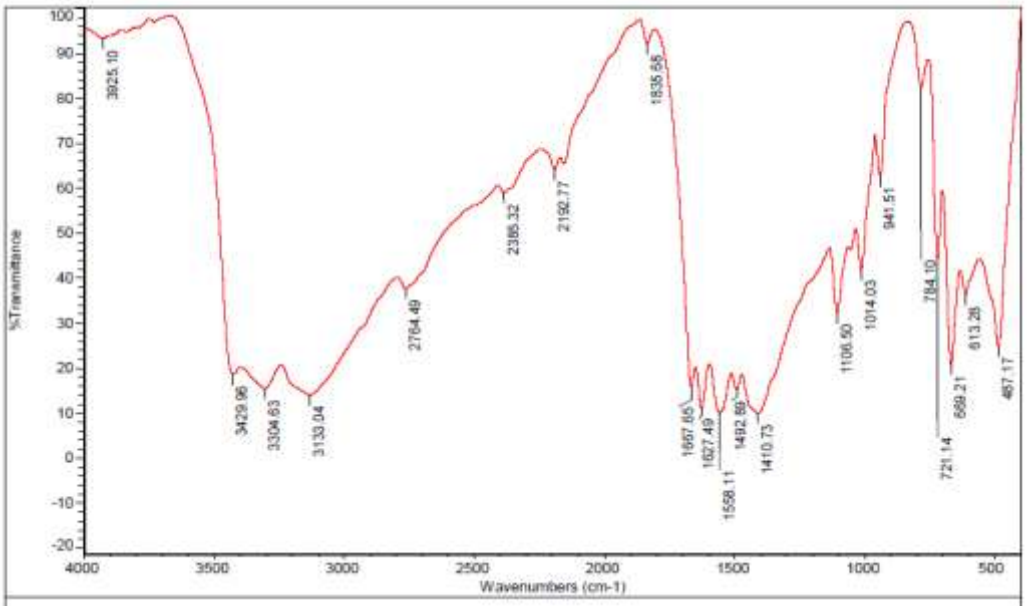


Fig. 7 FTIR spectrum of L cystein doped bis thiourea cadmium acetate

Table

Thiourea cm^{-1}(reported[17])	BTCA cm^{-1}	L-Cystein doped BTCA cm^{-1}	Assignment
469	486.42	487.17	S-C-N symmetric bending
640	621.52	613.28	S-C-N asymmetric bending
740	725.09	721.14	C=S symmetric stretching
1089	1110.28	1106.50	C=N symmetric stretching
1417	1411.93	1410.73	C=S asymmetric stretching
1472	1495.62	1492.89	C=N asymmetric stretching
1627	1628.45	1627.49	NH_2 bending
	1667.24	1667.65	NH_2 asymmetric stretching
3280	3304.84	3304.63	NH_2 asymmetric stretching
3100-3200	3131.73	3133.04	NH_2 symmetric stretching

Table3.Wavenumber assignment of thiourea, pure and Zn2+ doped BTCA

Thiourea is potentially capable of forming coordinate bonds through both sulphur and nitrogen. Both these possibilities can be explained by infrared spectra of the crystals. If the bonding is through sulphur, there

will be a decrease in the CS stretching frequency and an increase in the CN stretching frequency. The reverse happens if it is through nitrogen. [14].Both in pure and L-cystein doped bis thiourea cadmium acetate the CN stretching vibrations of thiourea are shifted to higher frequencies whereas, the CS stretching
vibrations of thiourea are shifted to lower frequencies.So it is evident that both BTCA and L-cystein doped BTCA form bonds through sulphur.

3.7 NLO studies

The non linear optical property of the grown crystal was determined using Kurtz and Perry method. A high intensity Q-switched mode locked Nd-YAG laser was used to generate about 1.13 mJ/pulse at the 1064nm fundamental radiation. The input laser beam with pulse duration 10 ns and frequency repetition 10 Hz is passed through the micro crystalline powdered sample packed in a capillary tube. The efficiency of the sample was compared with the micro crystalline powder of KDP as the reference material. The bride green emission (532 nm) from the specimen was collected a photomultiplier tube and finally measured on the storage oscilloscope (CRO) as output voltage. The second harmonic signal of 5mV and 8mV, respectively, were obtained for pure and doped BTCA with reference to KDP (19 mV).

IV. Conclusion

Good quality single crystal of pure and L-cystein doped BTCA was grown by slow evaporation technique under room temperature. Grown crystals were characterized and compared with pure BTCA. The recorded Powder X-ray diffraction pattern confirms the perfection of good quality single crystal. The CHN analysis reveals the presence of dopant in the grown crystal. Presence of all the elements and doping of L-cystein were confirmed by EDAX test. TGA and DTA analysis has revealed that thermal stability of doped BTCA is high compared to pure BTCA. The functional groups were verified using FTIR analysis. SHG conversion efficiency makes the crystal a latent material for NLO application.

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